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8,13-Diisopropyl-10,11-dimethyl-bis([1,3]dioxolo-[4′,5′:6,7]naphtho)[1,2-*d*;2,1-*f*][1,3]dioxepine

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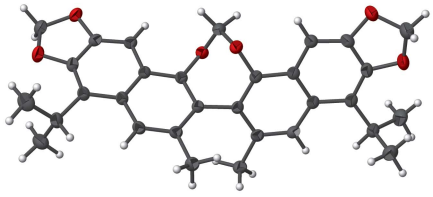
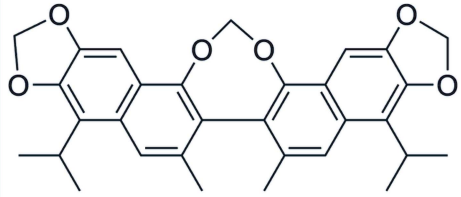
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{31}H_{30}O_6$, was obtained by protecting the six hydroxy groups of apogossypol by acetalization with dichloromethane. The molecule has a bridging dioxepine unit which hinders the rotation around the 2,2′-internaphthyl bond. The dihedral angle between the naphthyl units is 55.73 (3)°. In the crystal, very weak C—H···O interactions may help to consolidate the packing.

3D view



Chemical scheme



Structure description

The preparation of methylene acetals is a common method to protect vicinal OH groups (Wuts & Greene, 2007, Bonthrone & Cornforth, 1969). In case of the title compound **2**, called apogossypol trimethylene acetal, not only the hydroxy groups in the 6,7 and 6′,7′ position of apogossypol **1** but, due to the sterically related vicinity of the 1,1′-hydroxy groups to each other, these groups were also protected (Fig. 1). As a result of the formation of this seven-membered ring, the rotation around the 2,2′-internaphthyl bond is restricted and the angle between the planes defined by C1–C10 and C11–C20 is 55.73 (3)° (Fig. 2). The five-membered rings derived from the catechol-like diols show envelope conformations with the methylene carbon atoms (C21 and C23) as the flaps [fold angles between the OC_mO and OC_aC_aO (m = methylene, a = aromatic) fragments = 155.7 (2) and 161.4 (2)°, respectively]. In the crystal, two very weak C—H···O contacts from the C23 methylene group (Table 1) may help to consolidate the packing.

Synthesis and crystallization

25 mL dry DMSO and 0.42 mL (6.8 mmol) dry CH_2Cl_2 were placed under argon in a 100 mL quartz tube sealed with a Teflon screw cap with gas inlet port. The atmosphere

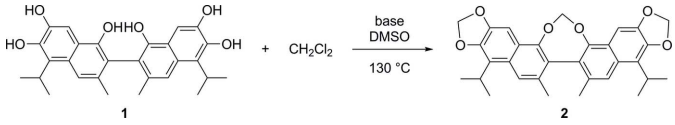


Figure 1
Reaction path for acetalization of apogossypol **1** with CH_2Cl_2 to apogossypol trimethylene acetal **2**.

was cautiously removed by stirring under vacuum and purging with argon (repeated three times). Then the mixture was heated to 130°C in an oil bath with stirring. When this temperature was reached, a solid mixture of 464 mg of apogossypol (1 mmol) and 655 mg of NaOtBu (6.8 mmol) was added in small portions under argon. The dark-brown mixture was allowed to stir for 16 h at 130°C. After cooling down to room temperature, it was poured into a tenfold volume of H_2O, whereupon a greyish brown solid precipitated. Isolation via preparative HPLC yielded 98 mg of an off-white solid (0.2 mmol, 20%). Crystals suitable for X-ray analysis were obtained from diethyl ether solution at room temperature.

m.p. 273°C.

^{1}H NMR (500 MHz, DMSO-d_6, δ in ppm): 1.42 (*d*, *J* = 6.8 Hz, 12H), 2.30 (*s*, 6H), 3.74 (*m*, *J* = 6.7 Hz, 2H), 5.65 (*s*, 2H), 6.11 (*s*, 4H), 7.30 (*s*, 2H), 7.85 (*s*, 2H).

^{13}C NMR (125 MHz, DMSO-d_6, δ in ppm): 19.8, 21.0, 21.2, 95.7, 100.7, 102.1, 120.3, 121.4, 122.0, 126.3, 129.0, 132.2, 145.3, 147.20, 147.23.

HRMS (ESI–TOF, *m*/*z*): $[M + H]^+$ 499.2123 calculated: 499.2120

Elemental analysis for $C_{31}H_{30}O_6$ (498.2 g mol^{-1}), calculated (found) in wt.-%: C 74.68 (74.42), H 6.07 (6.12).

IR (ATR, 32 scans, $\tilde{\nu}$ in cm^{-1}) 2957(*m*), 2926(*m*), 2877(*m*), 1614(*w*), 1441(*s*), 1347(*m*), 1310(*m*), 1298(*m*), 1241(*m*), 1224(*s*), 1168(*m*), 1121(*m*), 1102(*m*), 1073(*m*), 1044(*s*), 1016(*m*), 996(*m*), 980(*m*), 953(*s*), 933(*m*), 908(*m*), 881(*m*), 859(*s*), 785(*m*), 744(*m*), 731(*m*), 668(*m*), 636(*m*), 602(*m*), 568(*m*), 527(*m*), 422(*m*).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

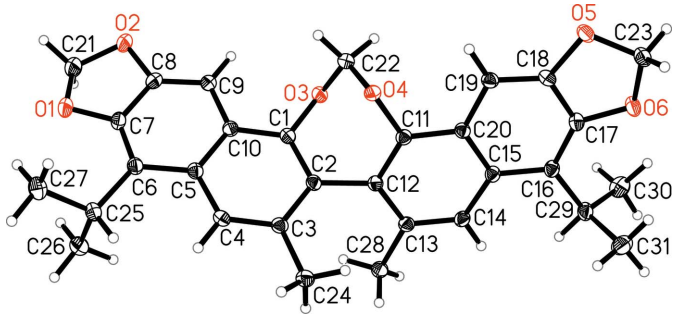


Figure 2
Molecular structure of the title compound with displacement ellipsoids drawn at the 30% probability level.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C23—H23*A*···O5^{i}	0.99	2.58	3.3956 (18)	140
C23—H23*B*···O4^{ii}	0.99	2.58	3.2442 (18)	124

Symmetry codes: (i) $-x+3, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{31}H_{30}O_6$
M_r	498.55
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, *b*, *c* (Å)	9.7053 (6), 11.0901 (7), 12.4156 (8)
α, β, γ (°)	68.0282 (16), 81.7012 (16), 86.4672 (16)
V (Å^3)	1226.25 (13)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.09
Crystal size (mm)	0.46 × 0.33 × 0.18
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.95, 0.98
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	43308, 5923, 4941
R_{int}	0.023
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.661
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.045, 0.138, 1.05
No. of reflections	5923
No. of parameters	340
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.50, −0.24

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *XP* in *SHELXTL* and *SHELXS97* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015) and *publCIF* (Westrip, 2010).

Acknowledgements

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full crystallographic data

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Crystal data

$C_{31}H_{30}O_6$
M_r = 498.55
Triclinic, $P\overline{1}$
a = 9.7053 (6) Å
b = 11.0901 (7) Å
c = 12.4156 (8) Å
α = 68.0282 (16)°
β = 81.7012 (16)°
γ = 86.4672 (16)°
V = 1226.25 (13) Å^3
Z = 2
$F(000)$ = 528
D_x = 1.350 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9929 reflections
θ = 2.8–30.6°
μ = 0.09 mm^{-1}
T = 150 K
Part of a plate, orange
0.46 × 0.33 × 0.18 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.95, T_{max} = 0.98
43308 measured reflections
5923 independent reflections
4941 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 28.0°, θ_{min} = 1.8°
h = −12→12
k = −14→14
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.138
S = 1.05
5923 reflections
340 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2 + 0.4119P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. All H atoms were placed in idealized positions with d(C—H) = 0.95–1.00 Å (CH), 0.99 (CH_2), 0.98 Å (CH_3) and refined using a riding model with U_{iso}(H) fixed at 1.2 U_{eq}(C) for CH, CH_2 and 1.5 U_{eq}(C) for CH_3.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.82699 (13)	0.25631 (12)	0.23443 (11)	0.0250 (3)
C2	0.76549 (13)	0.22345 (11)	0.34917 (11)	0.0241 (2)
C3	0.61762 (13)	0.21611 (12)	0.37149 (11)	0.0261 (3)
C4	0.54302 (13)	0.23621 (12)	0.27978 (11)	0.0264 (3)
H4	0.4443	0.2325	0.2958	0.032*
C5	0.60517 (13)	0.26203 (12)	0.16310 (11)	0.0252 (3)
C6	0.52512 (14)	0.27466 (12)	0.06984 (12)	0.0279 (3)
C7	0.60147 (14)	0.29242 (13)	−0.03592 (12)	0.0310 (3)
C8	0.74758 (15)	0.30407 (14)	−0.05803 (12)	0.0316 (3)
C9	0.82598 (14)	0.29600 (13)	0.02588 (11)	0.0288 (3)
H9	0.9243	0.3051	0.0098	0.035*
C10	0.75335 (13)	0.27314 (11)	0.13981 (11)	0.0248 (3)
C11	0.94951 (13)	0.31227 (12)	0.41291 (11)	0.0241 (2)
C12	0.85840 (13)	0.21138 (12)	0.43837 (11)	0.0240 (2)
C13	0.86743 (13)	0.10115 (12)	0.54305 (11)	0.0258 (3)
C14	0.96098 (14)	0.10164 (12)	0.61658 (11)	0.0272 (3)
H14	0.9651	0.0277	0.6866	0.033*
C15	1.05123 (13)	0.20650 (12)	0.59326 (11)	0.0249 (3)
C16	1.14992 (14)	0.20510 (12)	0.67065 (11)	0.0265 (3)
C17	1.22813 (13)	0.31411 (12)	0.63546 (11)	0.0266 (3)
C18	1.22056 (13)	0.42122 (12)	0.53020 (12)	0.0261 (3)
C19	1.13326 (13)	0.42565 (12)	0.45361 (11)	0.0265 (3)
H19	1.1302	0.4978	0.3821	0.032*
C20	1.04574 (13)	0.31570 (12)	0.48625 (11)	0.0239 (2)
C21	0.67417 (17)	0.2882 (2)	−0.21373 (14)	0.0475 (4)
H21A	0.6668	0.3455	−0.2959	0.057*
H21B	0.6843	0.1971	−0.2094	0.057*
C22	1.01188 (14)	0.39371 (14)	0.21042 (12)	0.0324 (3)
H22A	1.1140	0.3928	0.2104	0.039*
H22B	0.9894	0.4647	0.1381	0.039*
C23	1.36283 (15)	0.47149 (13)	0.63326 (13)	0.0329 (3)
H23A	1.4647	0.4831	0.6241	0.039*
H23B	1.3167	0.5232	0.6784	0.039*
C24	0.53967 (15)	0.19488 (15)	0.49121 (12)	0.0334 (3)
H24A	0.4524	0.2450	0.4830	0.050*
H24B	0.5969	0.2237	0.5358	0.050*
H24C	0.5190	0.1022	0.5326	0.050*

C25	0.36832 (14)	0.25869 (15)	0.08976 (13)	0.0337 (3)
H25	0.3333	0.2680	0.1661	0.040*
C26	0.33202 (18)	0.12209 (17)	0.10137 (15)	0.0454 (4)
H26A	0.3637	0.1103	0.0273	0.068*
H26B	0.2310	0.1104	0.1201	0.068*
H26C	0.3781	0.0578	0.1641	0.068*
C27	0.29569 (16)	0.36318 (17)	−0.00509 (15)	0.0431 (4)
H27A	0.3218	0.4495	−0.0107	0.065*
H27B	0.1946	0.3532	0.0152	0.065*
H27C	0.3242	0.3538	−0.0806	0.065*
C28	0.78370 (15)	−0.01978 (13)	0.57202 (12)	0.0321 (3)
H28A	0.8394	−0.0967	0.6103	0.048*
H28B	0.7583	−0.0236	0.4998	0.048*
H28C	0.6990	−0.0176	0.6248	0.048*
C29	1.16247 (16)	0.09451 (13)	0.78629 (12)	0.0340 (3)
H29	1.1097	0.0188	0.7884	0.041*
C30	1.31337 (18)	0.05092 (15)	0.80179 (14)	0.0426 (4)
H30A	1.3551	0.0262	0.7362	0.064*
H30B	1.3154	−0.0238	0.8755	0.064*
H30C	1.3662	0.1225	0.8036	0.064*
C31	1.09481 (18)	0.13534 (19)	0.88678 (14)	0.0481 (4)
H31A	1.1403	0.2137	0.8828	0.072*
H31B	1.1052	0.0649	0.9618	0.072*
H31C	0.9956	0.1535	0.8801	0.072*
O1	0.55313 (11)	0.30220 (11)	−0.13812 (9)	0.0404 (3)
O2	0.79134 (11)	0.32419 (12)	−0.17393 (9)	0.0414 (3)
O3	0.97105 (9)	0.27298 (9)	0.20978 (8)	0.0295 (2)
O4	0.94521 (9)	0.41888 (8)	0.30849 (8)	0.0278 (2)
O5	1.31535 (10)	0.51336 (9)	0.52047 (9)	0.0330 (2)
O6	1.32875 (11)	0.33807 (9)	0.69250 (9)	0.0336 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0229 (6)	0.0248 (6)	0.0275 (6)	−0.0008 (4)	−0.0039 (5)	−0.0095 (5)
C2	0.0255 (6)	0.0221 (5)	0.0258 (6)	−0.0024 (4)	−0.0046 (5)	−0.0093 (5)
C3	0.0274 (6)	0.0243 (6)	0.0270 (6)	−0.0044 (5)	−0.0015 (5)	−0.0101 (5)
C4	0.0234 (6)	0.0253 (6)	0.0307 (6)	−0.0034 (4)	−0.0024 (5)	−0.0105 (5)
C5	0.0265 (6)	0.0211 (5)	0.0282 (6)	−0.0013 (4)	−0.0060 (5)	−0.0083 (5)
C6	0.0270 (6)	0.0266 (6)	0.0297 (6)	−0.0006 (5)	−0.0073 (5)	−0.0085 (5)
C7	0.0325 (7)	0.0320 (7)	0.0276 (6)	−0.0011 (5)	−0.0107 (5)	−0.0075 (5)
C8	0.0332 (7)	0.0347 (7)	0.0230 (6)	−0.0018 (5)	−0.0028 (5)	−0.0064 (5)
C9	0.0256 (6)	0.0318 (6)	0.0266 (6)	−0.0018 (5)	−0.0038 (5)	−0.0077 (5)
C10	0.0259 (6)	0.0218 (6)	0.0256 (6)	−0.0004 (4)	−0.0048 (5)	−0.0071 (5)
C11	0.0258 (6)	0.0220 (6)	0.0233 (6)	0.0000 (4)	−0.0036 (5)	−0.0070 (5)
C12	0.0248 (6)	0.0248 (6)	0.0235 (6)	−0.0021 (4)	−0.0026 (4)	−0.0101 (5)
C13	0.0293 (6)	0.0235 (6)	0.0246 (6)	−0.0047 (5)	−0.0018 (5)	−0.0087 (5)
C14	0.0340 (7)	0.0235 (6)	0.0228 (6)	−0.0031 (5)	−0.0045 (5)	−0.0064 (5)

C15	0.0291 (6)	0.0230 (6)	0.0244 (6)	−0.0005 (5)	−0.0048 (5)	−0.0103 (5)
C16	0.0326 (6)	0.0231 (6)	0.0253 (6)	0.0002 (5)	−0.0072 (5)	−0.0094 (5)
C17	0.0284 (6)	0.0261 (6)	0.0285 (6)	0.0014 (5)	−0.0081 (5)	−0.0124 (5)
C18	0.0234 (6)	0.0229 (6)	0.0321 (6)	−0.0027 (4)	−0.0029 (5)	−0.0103 (5)
C19	0.0261 (6)	0.0232 (6)	0.0277 (6)	−0.0021 (5)	−0.0036 (5)	−0.0063 (5)
C20	0.0250 (6)	0.0220 (5)	0.0251 (6)	−0.0010 (4)	−0.0035 (5)	−0.0092 (5)
C21	0.0429 (9)	0.0684 (11)	0.0304 (8)	−0.0067 (8)	−0.0077 (6)	−0.0152 (7)
C22	0.0289 (6)	0.0376 (7)	0.0272 (6)	−0.0094 (5)	−0.0025 (5)	−0.0071 (5)
C23	0.0303 (7)	0.0305 (7)	0.0386 (7)	−0.0030 (5)	−0.0112 (6)	−0.0107 (6)
C24	0.0296 (6)	0.0419 (8)	0.0298 (7)	−0.0062 (6)	0.0008 (5)	−0.0154 (6)
C25	0.0267 (6)	0.0435 (8)	0.0318 (7)	−0.0026 (5)	−0.0069 (5)	−0.0134 (6)
C26	0.0417 (8)	0.0469 (9)	0.0433 (9)	−0.0145 (7)	−0.0093 (7)	−0.0085 (7)
C27	0.0325 (7)	0.0484 (9)	0.0479 (9)	0.0061 (6)	−0.0130 (6)	−0.0153 (7)
C28	0.0381 (7)	0.0271 (6)	0.0305 (7)	−0.0085 (5)	−0.0056 (5)	−0.0081 (5)
C29	0.0433 (8)	0.0274 (6)	0.0305 (7)	−0.0062 (6)	−0.0142 (6)	−0.0056 (5)
C30	0.0509 (9)	0.0321 (7)	0.0402 (8)	0.0095 (6)	−0.0125 (7)	−0.0073 (6)
C31	0.0428 (9)	0.0621 (11)	0.0313 (8)	−0.0035 (8)	−0.0034 (6)	−0.0082 (7)
O1	0.0369 (5)	0.0571 (7)	0.0278 (5)	−0.0021 (5)	−0.0118 (4)	−0.0135 (5)
O2	0.0380 (6)	0.0606 (7)	0.0227 (5)	−0.0051 (5)	−0.0055 (4)	−0.0106 (5)
O3	0.0223 (4)	0.0379 (5)	0.0281 (5)	−0.0021 (4)	−0.0028 (3)	−0.0119 (4)
O4	0.0289 (5)	0.0245 (4)	0.0261 (5)	−0.0035 (3)	−0.0055 (4)	−0.0037 (4)
O5	0.0303 (5)	0.0294 (5)	0.0379 (5)	−0.0079 (4)	−0.0102 (4)	−0.0075 (4)
O6	0.0378 (5)	0.0282 (5)	0.0381 (5)	−0.0032 (4)	−0.0166 (4)	−0.0114 (4)

Geometric parameters (Å, º)

C1—C2	1.3825 (18)	C21—O1	1.433 (2)
C1—O3	1.3959 (15)	C21—O2	1.4362 (19)
C1—C10	1.4098 (17)	C21—H21A	0.9900
C2—C3	1.4233 (17)	C21—H21B	0.9900
C2—C12	1.4900 (16)	C22—O4	1.4085 (17)
C3—C4	1.3779 (17)	C22—O3	1.4226 (17)
C3—C24	1.5075 (18)	C22—H22A	0.9900
C4—C5	1.4152 (18)	C22—H22B	0.9900
C4—H4	0.9500	C23—O6	1.4197 (17)
C5—C10	1.4290 (17)	C23—O5	1.4362 (17)
C5—C6	1.4453 (17)	C23—H23A	0.9900
C6—C7	1.362 (2)	C23—H23B	0.9900
C6—C25	1.5167 (18)	C24—H24A	0.9800
C7—O1	1.3801 (16)	C24—H24B	0.9800
C7—C8	1.4094 (19)	C24—H24C	0.9800
C8—C9	1.3502 (18)	C25—C26	1.526 (2)
C8—O2	1.3769 (16)	C25—C27	1.531 (2)
C9—C10	1.4241 (18)	C25—H25	1.0000
C9—H9	0.9500	C26—H26A	0.9800
C11—C12	1.3821 (17)	C26—H26B	0.9800
C11—O4	1.3939 (14)	C26—H26C	0.9800
C11—C20	1.4066 (17)	C27—H27A	0.9800

C12—C13	1.4219 (17)	C27—H27B	0.9800
C13—C14	1.3789 (17)	C27—H27C	0.9800
C13—C28	1.5091 (17)	C28—H28A	0.9800
C14—C15	1.4155 (17)	C28—H28B	0.9800
C14—H14	0.9500	C28—H28C	0.9800
C15—C20	1.4293 (17)	C29—C30	1.530 (2)
C15—C16	1.4470 (17)	C29—C31	1.530 (2)
C16—C17	1.3604 (18)	C29—H29	1.0000
C16—C29	1.5149 (18)	C30—H30A	0.9800
C17—O6	1.3777 (15)	C30—H30B	0.9800
C17—C18	1.4070 (18)	C30—H30C	0.9800
C18—C19	1.3479 (18)	C31—H31A	0.9800
C18—O5	1.3771 (15)	C31—H31B	0.9800
C19—C20	1.4252 (17)	C31—H31C	0.9800
C19—H19	0.9500		

C2—C1—O3	118.53 (11)	O4—C22—O3	112.29 (10)
C2—C1—C10	124.07 (11)	O4—C22—H22A	109.1
O3—C1—C10	117.40 (11)	O3—C22—H22A	109.1
C1—C2—C3	117.75 (11)	O4—C22—H22B	109.1
C1—C2—C12	117.17 (11)	O3—C22—H22B	109.1
C3—C2—C12	124.79 (11)	H22A—C22—H22B	107.9
C4—C3—C2	119.11 (11)	O6—C23—O5	107.43 (10)
C4—C3—C24	118.90 (12)	O6—C23—H23A	110.2
C2—C3—C24	121.90 (11)	O5—C23—H23A	110.2
C3—C4—C5	123.69 (12)	O6—C23—H23B	110.2
C3—C4—H4	118.2	O5—C23—H23B	110.2
C5—C4—H4	118.2	H23A—C23—H23B	108.5
C4—C5—C10	117.31 (11)	C3—C24—H24A	109.5
C4—C5—C6	122.60 (12)	C3—C24—H24B	109.5
C10—C5—C6	120.08 (12)	H24A—C24—H24B	109.5
C7—C6—C5	115.21 (12)	C3—C24—H24C	109.5
C7—C6—C25	121.96 (12)	H24A—C24—H24C	109.5
C5—C6—C25	122.65 (12)	H24B—C24—H24C	109.5
C6—C7—O1	127.54 (13)	C6—C25—C26	110.01 (12)
C6—C7—C8	124.16 (12)	C6—C25—C27	112.64 (12)
O1—C7—C8	108.30 (12)	C26—C25—C27	111.63 (12)
C9—C8—O2	128.09 (13)	C6—C25—H25	107.4
C9—C8—C7	122.49 (12)	C26—C25—H25	107.4
O2—C8—C7	109.42 (12)	C27—C25—H25	107.4
C8—C9—C10	116.41 (12)	C25—C26—H26A	109.5
C8—C9—H9	121.8	C25—C26—H26B	109.5
C10—C9—H9	121.8	H26A—C26—H26B	109.5
C1—C10—C9	120.48 (11)	C25—C26—H26C	109.5
C1—C10—C5	117.89 (11)	H26A—C26—H26C	109.5
C9—C10—C5	121.59 (11)	H26B—C26—H26C	109.5
C12—C11—O4	118.23 (11)	C25—C27—H27A	109.5
C12—C11—C20	124.36 (11)	C25—C27—H27B	109.5

O4—C11—C20	117.41 (10)	H27A—C27—H27B	109.5
C11—C12—C13	117.62 (11)	C25—C27—H27C	109.5
C11—C12—C2	116.91 (11)	H27A—C27—H27C	109.5
C13—C12—C2	125.32 (11)	H27B—C27—H27C	109.5
C14—C13—C12	119.25 (11)	C13—C28—H28A	109.5
C14—C13—C28	119.01 (11)	C13—C28—H28B	109.5
C12—C13—C28	121.62 (11)	H28A—C28—H28B	109.5
C13—C14—C15	123.47 (11)	C13—C28—H28C	109.5
C13—C14—H14	118.3	H28A—C28—H28C	109.5
C15—C14—H14	118.3	H28B—C28—H28C	109.5
C14—C15—C20	117.46 (11)	C16—C29—C30	112.64 (12)
C14—C15—C16	122.87 (11)	C16—C29—C31	109.28 (12)
C20—C15—C16	119.64 (11)	C30—C29—C31	110.71 (12)
C17—C16—C15	115.30 (11)	C16—C29—H29	108.0
C17—C16—C29	121.16 (11)	C30—C29—H29	108.0
C15—C16—C29	123.47 (11)	C31—C29—H29	108.0
C16—C17—O6	127.12 (12)	C29—C30—H30A	109.5
C16—C17—C18	124.26 (12)	C29—C30—H30B	109.5
O6—C17—C18	108.60 (11)	H30A—C30—H30B	109.5
C19—C18—O5	127.98 (12)	C29—C30—H30C	109.5
C19—C18—C17	122.69 (11)	H30A—C30—H30C	109.5
O5—C18—C17	109.32 (11)	H30B—C30—H30C	109.5
C18—C19—C20	116.05 (11)	C29—C31—H31A	109.5
C18—C19—H19	122.0	C29—C31—H31B	109.5
C20—C19—H19	122.0	H31A—C31—H31B	109.5
C11—C20—C19	120.23 (11)	C29—C31—H31C	109.5
C11—C20—C15	117.76 (11)	H31A—C31—H31C	109.5
C19—C20—C15	122.01 (11)	H31B—C31—H31C	109.5
O1—C21—O2	106.62 (12)	C7—O1—C21	105.23 (11)
O1—C21—H21A	110.4	C8—O2—C21	104.42 (11)
O2—C21—H21A	110.4	C1—O3—C22	112.20 (10)
O1—C21—H21B	110.4	C11—O4—C22	112.54 (10)
O2—C21—H21B	110.4	C18—O5—C23	105.17 (10)
H21A—C21—H21B	108.6	C17—O6—C23	106.00 (10)

O3—C1—C2—C3	175.54 (10)	C13—C14—C15—C16	−179.34 (12)
C10—C1—C2—C3	−5.07 (19)	C14—C15—C16—C17	−179.62 (12)
O3—C1—C2—C12	1.47 (17)	C20—C15—C16—C17	2.43 (18)
C10—C1—C2—C12	−179.13 (11)	C14—C15—C16—C29	−2.7 (2)
C1—C2—C3—C4	2.77 (18)	C20—C15—C16—C29	179.38 (12)
C12—C2—C3—C4	176.34 (11)	C15—C16—C17—O6	179.85 (12)
C1—C2—C3—C24	−173.52 (12)	C29—C16—C17—O6	2.8 (2)
C12—C2—C3—C24	0.05 (19)	C15—C16—C17—C18	−2.0 (2)
C2—C3—C4—C5	1.10 (19)	C29—C16—C17—C18	−179.06 (12)
C24—C3—C4—C5	177.50 (12)	C16—C17—C18—C19	0.2 (2)
C3—C4—C5—C10	−2.82 (18)	O6—C17—C18—C19	178.63 (12)
C3—C4—C5—C6	176.00 (12)	C16—C17—C18—O5	−178.74 (12)
C4—C5—C6—C7	−176.55 (12)	O6—C17—C18—O5	−0.33 (15)

C10—C5—C6—C7	2.23 (18)	O5—C18—C19—C20	179.94 (12)
C4—C5—C6—C25	−1.22 (19)	C17—C18—C19—C20	1.19 (19)
C10—C5—C6—C25	177.56 (12)	C12—C11—C20—C19	−178.50 (12)
C5—C6—C7—O1	177.26 (12)	O4—C11—C20—C19	0.63 (17)
C25—C6—C7—O1	1.9 (2)	C12—C11—C20—C15	1.13 (19)
C5—C6—C7—C8	−2.8 (2)	O4—C11—C20—C15	−179.73 (11)
C25—C6—C7—C8	−178.14 (13)	C18—C19—C20—C11	178.95 (12)
C6—C7—C8—C9	1.3 (2)	C18—C19—C20—C15	−0.67 (18)
O1—C7—C8—C9	−178.72 (13)	C14—C15—C20—C11	1.14 (18)
C6—C7—C8—O2	−178.55 (13)	C16—C15—C20—C11	179.20 (11)
O1—C7—C8—O2	1.42 (16)	C14—C15—C20—C19	−179.23 (11)
O2—C8—C9—C10	−179.36 (13)	C16—C15—C20—C19	−1.18 (19)
C7—C8—C9—C10	0.8 (2)	C7—C6—C25—C26	76.33 (16)
C2—C1—C10—C9	−174.57 (12)	C5—C6—C25—C26	−98.68 (15)
O3—C1—C10—C9	4.83 (17)	C7—C6—C25—C27	−48.91 (18)
C2—C1—C10—C5	3.33 (19)	C5—C6—C25—C27	136.07 (14)
O3—C1—C10—C5	−177.27 (10)	C17—C16—C29—C30	−50.79 (18)
C8—C9—C10—C1	176.59 (12)	C15—C16—C29—C30	132.44 (14)
C8—C9—C10—C5	−1.23 (19)	C17—C16—C29—C31	72.70 (17)
C4—C5—C10—C1	0.65 (17)	C15—C16—C29—C31	−104.07 (15)
C6—C5—C10—C1	−178.19 (11)	C6—C7—O1—C21	−166.34 (15)
C4—C5—C10—C9	178.53 (11)	C8—C7—O1—C21	13.69 (16)
C6—C5—C10—C9	−0.31 (18)	O2—C21—O1—C7	−23.43 (17)
O4—C11—C12—C13	177.72 (11)	C9—C8—O2—C21	164.34 (16)
C20—C11—C12—C13	−3.15 (19)	C7—C8—O2—C21	−15.81 (16)
O4—C11—C12—C2	1.94 (17)	O1—C21—O2—C8	24.11 (17)
C20—C11—C12—C2	−178.93 (11)	C2—C1—O3—C22	−76.37 (14)
C1—C2—C12—C11	49.07 (16)	C10—C1—O3—C22	104.20 (12)
C3—C2—C12—C11	−124.53 (13)	O4—C22—O3—C1	46.28 (14)
C1—C2—C12—C13	−126.35 (13)	C12—C11—O4—C22	−77.59 (14)
C3—C2—C12—C13	60.04 (18)	C20—C11—O4—C22	103.22 (13)
C11—C12—C13—C14	2.84 (18)	O3—C22—O4—C11	47.28 (14)
C2—C12—C13—C14	178.23 (12)	C19—C18—O5—C23	170.18 (13)
C11—C12—C13—C28	−173.25 (12)	C17—C18—O5—C23	−10.94 (14)
C2—C12—C13—C28	2.1 (2)	O6—C23—O5—C18	18.06 (14)
C12—C13—C14—C15	−0.7 (2)	C16—C17—O6—C23	−170.02 (14)
C28—C13—C14—C15	175.52 (12)	C18—C17—O6—C23	11.63 (14)
C13—C14—C15—C20	−1.35 (19)	O5—C23—O6—C17	−18.38 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C23—H23*A*···O5^{i}	0.99	2.58	3.3956 (18)	140
C23—H23*B*···O4^{ii}	0.99	2.58	3.2442 (18)	124

Symmetry codes: (i) −*x*+3, −*y*+1, −*z*+1; (ii) −*x*+2, −*y*+1, −*z*+1.